THE LEAD/ACID BATTERY INDUSTRY IN JAPAN

K. SHIMIZU

The Furukawa Battery Co., Ltd., 2-16-1 Hoshikawa, Hodogaya-ku, Yokohama 240 (Japan)

Introduction

Japan ranks second to the U.S.A. in the free world in lead/acid battery manufacturing. This is a result of the rapid growth in production volume resulting from acceleration of equipment investment and reduction in manpower to meet the market demand.

Furthermore, there has been an explosion in both demand and production within recent years. Keeping pace with the wide diversity of customer requirements, a demanding schedule has been initiated in order to promote high-energy-density battery development. The development and production of maintenance-free, sealed batteries of small volume and low weight for miniature cordless power sources has also started in response to the increased needs of industry.

As a result of advances in materials and production processes, dramatic technical improvements in a wide variety of automotive and industrial lead/acid batteries have been implemented. In the case of automotive batteries, the major new refinements have been:

(i) substantial reduction in size and weight;

(ii) maintenance-free systems due to the use of low-antimony and calcium-lead alloy grids.

Manufacturers of stationary batteries are also heavily committed to maintenance-free systems by use of catalyst vent-cap apparatus.

More recently, in response to market demands, recombinant electrolyte technology has been actively pursued. Also, high performance, smaller, sealed lead/acid batteries that do not leak (even if they are turned sideways or upside-down) and do not require water additions are now commercially available in a rapidly expanding market. The reasons why these types of battery are widely utilized is because the units have uniform quality, are highly reliable, and are relatively cost effective.

Table 1 shows the yearly total production costs of primary and secondary batteries in 1985 [1]. It can be seen that primary and secondary batteries constitute 32% and 68% of the total production costs, respectively. Amongst secondary types, the production costs of lead/acid systems are more than three times those of alkaline systems. The yearly production volumes of lead/acid batteries in Japan during the period 1982 - 1986 are given in Table 2 [2].

TABLE 1										
Total product	tion cost of I	primary and	secondary lea	d/acid batte	ries in Japan	in 1985 [1]				
Battery type		Classificatior		To	otal cost	Amo	ount (¥)	Ma	nufacturing	cost
				%)	((bill	ions)	Sul	ototal	Total
Primary	1	Manganese di Albaline man	ry cell	18 7		71.	99	127	0.7	
		Silver-oxide/	zine cell	- 4 (15.	ດມຸດ	(32	(%)	396.7
		Uther cells	*	י גא ו		12.	، ن ډ		Ľ	
secondary		Lead-acid bé Alkaline batt	attery*	10		204. 65.	1* 6	268)	9.7 (%)	
reau/aciu patrier	y production vi		In Japan, by yes	r [2]	, oo ,		1001			
Battery type	1982		1983		1984		1985		1986	
	Lead consumption (ton)	Amount (thousands yen)	Lead consumption (ton)	Amount (thousands yen)	Lead consumption (ton)	Amount (thousands yen)	Lead consumption (ton)	Amount (thousands yen)	Lead consumption (ton)	Amount (thousands yen)
Four-wheeled vehicle battery	174 379	118 667 333	195 248	111 349 873	220 378	124 643 688	229 909	140 706 927	226 776	146 810 112
Motorcycle	13 279	14 789 125	$12 \ 394$	13 971 288	11 095	13 102 029	12 190	11 755 856	10 545	13 440 352
Stationary	8 420	$14\ 952\ 088$	8 361	14 962 269	9 100	15 486 367	9 822	$16\ 493\ 646$	11 082	17 840 565
Portable	923	$2\ 450\ 031$	736	1 113 479	658	873 569	439	789 765	400	517 469
Traction	9 367	7 715 507	10770	7 577 482	12 202	8 618 900	13531	9547518	13 279	10 017 828
Railway	1 206	$1\ 202\ 471$	666	$1 \ 025 \ 625$	836	846 796	784	749 128	592	854 590
Other types	4 146	$4\ 064\ 695$	5462	6746611	6 858	$9 \ 160 \ 124$	9 808	12 120 667	15 669	14 712 820
Total	211 720	163 841 250	233 970	156746627	261 127	172 731 473	276483	192 163 507	278 343	204 193 736

34

Automotive lead/acid batteries

Approximately 80% of the total output of Japanese lead/acid batteries are used in automobiles. Compared with other types, the production process of automotive batteries is relatively easy; fully automatic machines are used and are based on the concept of a rapid and large-scale, high-volume manufacturing system. Figure 1 shows the flowchart of a continuous automotive battery manufacturing line. With advances in production machine capabilities, the overall manufacturing process for full automation has been steadily improved. The major improvements have been:



Fig. 1. Automotive lead/acid battery manufacturing process.

(i) highly efficient grid-production systems, such as casting technology using an automotive grid casting machine, expanding metal technology and punching metal technology;

(ii) continuous processing from paste mixing to paste application;

(iii) development of stacking machines for automatically assembling plate groups and separators;

(iv) automatic methods for group stacking, or welding, to the battery assembly stage;

(v) highly effective joining of the cover to the container by heat sealing techniques;

(vi) automatic techniques for in-container formation.

In addition, batteries have been made more efficient and maintenance-free, and there have been sayings in both size and volume of the units. To cut back the fuel consumption of cars, improve their viability and achieve cost reduction, much of the intensive developmental effort has been devoted to achieving more power from the battery within the same space configuration. In particular, cranking power has been upgraded. For these reasons, there has been a reduction in the lead content of the grids, an increase in the amount of plastic used in the container, and a shift towards the use of composite grid materials (*i.e.*, lead-plastic composites). A drop in internal resistance has also been effected through reduction in the thickness of both the plates and the separators. Table 3 provides a comparison of the characteristics of high performance, thin separators and conventional types [3]. At present, low electrical resistance polyethylene and plastic separators are both used in automotive batteries. These types feature a high degree of efficiency in output power characteristics and cold-cranking performance. They also provide savings in size and volume. The low electrical resistance separators of Table 3 consist of insulator material with good acid resistance and oxidation resistance and are used in combination with excellent fibrous, acid-resistant glass-mats.

TABLE 3

Separator type	Impregnated cellulose fibre	Microporous rubber	Sintered PVC	Low resistance polyethylene	Resin fibre
Thickness (mm)	0.5 - 1.0	0.4 - 1.0	0.5 - 0.2	0.1 - 0.2	$0.1 \cdot 0.4$
Electrical resistance $(\Omega \text{ dm}^{-2}/\text{sheet})$	0.0012 - 0.003	0.0012 - 0.003	0.0012 - 0.003	0.0002 - 0.0004	0.0002 - 0.0006
Degree of acid resistance (h/sheet)	40 - 70	100 - 500	50 - 100	100 - 120	100 - 200
Pore size (μ)	20 - 30	0.5 - 5	20 - 40	0.1 - 1	< 10
Porosity (%)	60	55	55	60	60

Separator characteristics [3]



Fig. 2. Water loss from batteries,

To date, an antimony-lead alloy has been used for the battery grids. When close to the end-of-charge, the use of this alloy causes acceleration of water decomposition, acid reduction, and an increase in water addition. Lead alloys that qualify for use in automotive batteries as maintenance-free systems generally fall into two classifications: low antimony-lead (3 wt.% Sb) and calcium-lead $(0.08 \cdot 0.12 \text{ wt.\% Ca})$. In Japan, automotive batteries sold as maintenance free include low-antimony batteries. These batteries require no maintenance, such as water addition. Figure 2 compares the water loss between maintenance-free and standard batteries. The maintenance-free battery using a lead-calcium alloy exhibits water loss only within the range of the upper and lower lines, even if the battery provides a service of 100 000 km. Thus, there is no need to add water until the battery nears the end of its useful life.

Figure 3 shows the self-discharge characteristics of batteries, *i.e.*, acid s.g. *versus* stand time. The self-discharge rate of the lead-calcium battery is more than three times smaller than that of the standard lead-antimony type, thus allowing the former to be stored for long periods.

The progressive savings in the size and the volume of automotive batteries are illustrated in Fig. 4 [4]. The relationship between cranking capability and low-rate discharge capacity imposes a limitation on the reduction in weight and size that can be achieved. The use of electronic controls



Fig. 3. Self-discharge characteristics of batteries.



Fig. 4. Savings in size and volume of automotive batteries. W/kg is for discharge to 8 V. Upper notation refers to battery type; notation in parentheses to overall size. Solid line provides example of battery with 127 mm overall width; broken line for battery with 171 mm overall width.

and the increase in the number of car air-conditioners, audio amplifiers and electric motors have increased the requirement for low-rate discharge characteristics.

The market demand for maintenance-free batteries is shown in Fig. 5 [4]. Positive plates consisting of a lead-calcium alloy tend to yield sudden capacity loss when subjected to deep-discharge, discharge cycle service, or high temperatures. Currently, hybrid battery plates consisting of low-antimony-alloy positive grids and lead-calcium alloy negative grids are being used in increasing numbers.

Recently, some battery manufacturers have begun to market sealed batteries aiming at qualifying them as truly maintenance free. These products give true maintenance-free and position-free operation, as well as providing savings in both size and volume. If any new advantages are determined, *e.g.*, as a result of new vehicular design modifications, it is considered that batteries of this type will be in widespread use as automotive types. Totally maintenance-free and position-free motorcycle battery production and sales have already been implemented.



Fig. 5. Trends in the application of maintenance-free automotive batteries.

Industrial lead/acid batteries

Industrial lead/acid batteries fall into two major categories, namely, stationary batteries and traction batteries.

A summary of the technological changes over the past two decades includes:

(i) switching from hard rubber or glass to plastic container material; this results in small savings in size and volume;

(ii) increased use of catalyst vent caps for maintenance-free operation;

(iii) improved high-rate discharge batteries have been developed.

These concepts have long lead-times before entering the market, and thereby have a history of proven reliability. However, several years ago, and unlike the catalyst vent-cap battery, a gas-recombination sealed lead/acid battery rapidly entered the industrial battery field.

In brief, the air-tight principle of the sealed lead/acid battery is as follows. During charging, traditional types of lead/acid batteries evolve oxygen at the positive plate and hydrogen at the negative plate. The following equations show the reactions taking place:

positive electrode:
$$H_2O \longrightarrow \frac{1}{2}O_2 + 2H^+ + 2e^-$$
 (1)

negative electrode: $2H^+ + 2e^- \longrightarrow H_2$

When the water level falls below the top of the negative plates (resulting in a dried plate), oxygen is reduced to water there and results in sulphation of the negatives, *i.e.*,

$$2Pb + O_2 + 2H_2SO_4 \longrightarrow 2PbSO_4 + 2H_2O$$
(3)

Thus, it can be seen that oxygen evolved at the positive plate is adsorbed at the negative plate and reacts to form lead sulphate which, in turn, is reduced to lead. This is the reason why the negative plate is free from any hydrogen generation and the air-tight construction ensures gas recombination. The latter involves "no free acid" and the rapid diffusion of oxygen from the positive to the negative plate or the partial exposure of the negative surface. The grid alloy of the sealed lead/acid battery is a lead-calcium alloy in both the positive and negative plates to ensure a lower self-discharge rate. Very fine, fibrous, glass woven separators with good acid-resistance and very low electrical-resistance are impregnated with the required amount of acid. The woven fibrous-glass separator has not only a large porosity (about 90%) and an excellent acid retention, but also very low electrical resistance. This results in a vertically 'no free acid' system. These conditions facilitate the diffusion of oxygen from the positive plate to the negative plate. The gas-recombination lead/acid battery specifications shown in Table 4 were established in 1982 [5]. Table 5 shows the specifications established in 1987 by the Japan Storage Battery Association [5].

The HSE series batteries (Table 4) are already commercially available. In order to improve the scale-up of cells and give longer life and higher performance, the MSE series batteries (Table 5) have also been developed.

(2)

Battery type	Voltage	Capacity (.	Ah)	Overall	dimensio	ns (mm)		
	(V)	C/10 rate	C/1 rate	Overall height	Height (±3)	Width (±3)	Length (±3)	Weight (kg)
HSE-30-12	12	30	18	220	190	128	235	13
HSE-40-12	12	40	24	220	190	128	299	16.5
HSE-50-12	12	50	30	220	190	128	363	20
HSE-60-6	6	60	36	220	190	128	217	12.5
HSE-80-6	6	80	48	220	190	128	281	16
HSE-100-6	6	100	60	220	190	128	345	19.5

TABLE 4

1982 specifications for gas-recombination, small, sealed, stationary lead/acid batteries [5]

TABLE 5

1987 specifications for gas-recombination, sealed, stationary, lead/acid batteries [5]

Battery type	Voltage	Capacity	(A h)	Overall d	limension	s (mm)		
	(V)	C/10 rate	C/1 rate	Overall height	Height (±3)	Width (±3)	Length (±3)	Weight (kg)
MSE-150	2	150	97.5	365	330	170	106	15
MSE-200	2	200	130	365	330	170	106	17.5
MSE-300	2	300	195	365	330	170	150	25
MSE-500	2	500	325	365	330	171	241	41
MSE-1000	2	1000	650	365	330	171	471	80

The latter types have positive and negative pasted plates and are intended to upgrade the high-rate discharge characteristics. A lead-calcium grid alloy is employed. In order to reduce the stress on the positive grid, active material optimization has been implemented. Separators use 85% microporous sodalime glass, short-stock mat. The containers and lids are made from ABS resin. Unlike catalyst vent-cap batteries, gas-recombination types feature:

(i) no need to add water, to take acid gravity readings, or to provide an equalization charge;

(ii) relative safety from liquid leakage due to acid immobilization, even if the container or cover is damaged;

(iii) less space due to savings in size and volume;

(iv) no need for component replacements with resulting longer battery life;

(v) lower self-discharge rate, 0.1% or less per day at 20 °C.

As a result of these favourable aspects, work has commenced into the development of large sized gas-recombination cells, *i.e.*, in the 2000 A h to 3000 A h range.

Small sealed lead/acid batteries

Recently, increased demands for portable power equipment have stimulated the market for batteries with a high density paste that will provide deep-cycle service for long periods of time. Table 6 shows the specifications for such batteries that were established in 1986 by the Japan Storage Battery Association [5].

Battery	Voltage	C/20	Overall dime	ensions (mm)		Weight
type	(V)	capacity (A h)	Length	Width	Height	(g)
6M 1.0	6	1.0	51 ± 2	42 ± 2	51 ± 2	280
6M 1.2	6	1.2	51 ± 2	24 ± 2	97 ± 2	310
6M 2.0	6	2.0	53 ± 2	51 ± 2	75 ± 2	480
6M 3.0	6	3.0	60 ± 2	34 ± 2	134 ± 2	680
6M 3.2	6	3.2	124 ± 3	33 ± 3	66 ± 2	720
6M 4.0	6	4.0	102 ± 2	48 ± 2	70 ± 2	860
6M 6.0	6	6.0	94 ± 2	33.5 ± 2	151 ± 2	1250
6M 7.0	6	7.0	118 ± 2	56 ± 2	98 ± 2	1430
6M 8.0	6	8.0	94 ± 2	50 ± 2	151 ± 2	1800
6M10	6	10	94 ± 2	50 ± 2	151 ± 2	2000
6M20	6	20	125 ± 2	83 ± 2	157 ± 2	3700
12M 0.7	12	0.7	61.5 ± 2	25 ± 2	96 ± 2	350
12M 1.2	12	1.2	52 ± 3	49 ± 3	98 ± 3	580
12M 1.9	12	1.9	60 ± 2	34 ± 2	178 ± 2	840
12M 3.0	12	3.0	60 ± 2	67 ± 2	134 ± 1	1300
12M 3.2	12	3.2	70 ± 2	47 ± 2	195 ± 2	1300
12M 6.0	12	6.0	94 ± 2	65 ± 2	151 ± 2	2300
12M15	12	15	167 ± 2	76 ± 2	181 ± 2	5900
12M24	12	24	125 ± 2	166 ± 2	175 ± 2	9000

TABLE 6

1986 specifications for small sealed lead/acid batteries [5]

The sales of small, sealed, lead/acid batteries in Japan during 1970 and 1985 are shown in Fig. 6 [4]. It can be seen that a particularly rapid growth has been experienced since 1982. In 1985, shipments amounted to 56 202 208 cells.

Changes in the size and weight of small, sealed, lead/acid batteries for portable devices are demonstrated by the data given in Fig. 7 [6]. It can be seen that a marked improvement has particularly been achieved in terms of volumetric energy density.

In recent times, there have been increasing requests for shorter charging times. This has been achieved by the use of thinner plates. Instead of housing rectangular-type batteries in the battery room within the conventional electrical system, portable appliances are equipped with a cartridge-type, thin battery pack located in the back of the equipment. These batteries are flat-



Fig. 6. Annual sales of small, sealed, lead/acid batteries in Japan.

Fig. 7. Trends in gravimetric and volumetric energy density (C/1 rate) of small, sealed, lead/acid batteries in Japan.

plate types that use a laminated plastic film bag.

Possible future technical problems with sealed lead/acid batteries include:

(i) compact and light-weight: improvement in the active material utilization ratio, acid retention, development of corrosion-resistant grids, practical application of plastic grids;

(ii) refinement of charge-acceptance characteristics after over-discharge and/or over-charge, including reduction of the resistance of the oxidized thin film produced at the positive-grid/active-material interface;

(iii) improvement in battery life.

Electric vehicle batteries

Electric vehicle batteries are now in the process of being developed; the work is being directed by the Electric Vehicle Engineering Research Association (EVERA). Table 7 shows the advanced lead/acid battery specification and the performance of single cells [7].

Test data from a prototype vehicle are given in Table 8 [7]. Advanced lead/acid batteries have provided a greater range (100 - 105 km) than the targeted figure (98 - 100 km). Future battery work will be directed towards the development of a maintenance-free system.

Load-levelling batteries

In April 1981, work commenced on a load-levelling facility using alternative advanced batteries. This activity formed part of the "Moon-

[~
Ξ
닀
7
F

	<u> </u>
	5
	nce
	rma
	rfoi
	l pe
	[e]
	igle
	l sir
	anc
	suc
	cati
	plid
	e ap
	nicl
	: vel
	tric
	elec
	for
	SU
	atio
	ific
	bec
	ry s
	atte
	d b
	/aci
	ead
•	ed l
	anc
	Adv
	4

TABLE /									
Advanced lead/ac	id battery speci	fications for ele	ectric vehic	ele applicat	ions and si	ingle-cell pe	rformance [7]		
Specification: Single unit							Battery pack		
Nominal voltage	No. of cells	Capacity ^a	Overall si	zes (mm)		Weight ^b	Total voltage	Quantity	Total weight
(v)		(4 h)	Length	Width	Height	(kg)	(V)		(kg)
12	9	150	502	180	257	40	96	8	320
Single unit perfor Target	mance:	Results							
Energy density (W h kg ⁻¹)	Life (cycle)	Capacit (A h)	y ^a	Average (V)	voltage ^a	Weigł (kg)	at ^b Ene (W	rgy density ^a h kg ⁻¹)	Life ^c (cycle)
45	1250	155		11.8		40.0	45.	6	1310
^a C/5 rate.									

^bFilled, including bolts and nuts. c60% DOD.

TABLE 8

Test results of prototype electric vehicle

Parameter	Target	Achieved per	formance		Remarks
		Ni/Zn	Ni/Fe	Advanced Pb/acid	
Range per charge (km) (Advanced battery)	170 - 190	170 - 200	190 - 200	_	Constant speed 40 km h ⁻¹
Range per charge (km) (Advanced Pb/acid)	98 - 100			100 - 105	Constant speed 40 km h ⁻¹
Top speed $(km h^{-1})$	80	90	85	85 - 90	0 - 40 km h ¹
Acceleration (s)	7.5 - 8.5	7.0 - 7.5	8.0 - 8.5	7.5 - 8.0	
Gradeability					
— Maximum grade (%)	25	> 25	> 25	> 25	_
-7% grade climbing speed (km h ⁻¹)	40 - 45	> 45	> 40	> 45	
Overall weight (kg)	$1390 \cdot 1420$	1420 - 1456	$1440 \cdot 1496$	1400 - 1415	—



Fig. 8. Development schedule for load-levelling batteries.

light" project to which approximately 17 000 million yen has been committed over 11 years. Figure 8 shows the development schedule for these batteries [8].

Alternative advanced batteries for load-levelling applications fall into four categories: sodium/sulphur, zinc/chlorine, zinc/bromine, and redox type. In the Fall of 1986, a 10 kW load-levelling battery was tested and evaluated, and in the Fall of 1987, a 60 kW battery will be assessed. When using an advanced lead/acid battery, testing and evaluation is conducted with a systems engineering approach. In this regard, since the Fall of 1986, a 1000 kW lead/acid battery has been operated and tested. As a result of making refinements to standard lead/acid batteries, this loadlevelling battery features higher energy and power density, easier maintenance, and improved reliability. Currently, the verification tests are being performed at the Kansai Electric Power Co., Ltd. Table 9 shows the facility specifications [9]. The battery consists of 526 series-connected cells, resulting in a high voltage type. It is 125 cm high and weighs 560 kg.

TABLE 9

Specifications of advanced lead/acid battery bank for load levelling [9]

Facility sp Nominal	ecifications – No. series-	- tubular plate b No. rows	attery, weight Battery bod	filled ~560 y) kg		
voltage (V)	connected cells	for batteries	Nominal capacity (A h) ^a	Width (mm)	Length (mm)	Container height (mm)	Overall height (mm)
1052	526	One row (8 divisions)	7500	505	375	1150	1250

 $^{a}C/10$ rate.

Conclusions

Over the past ten years, the automobile industry has experienced a 6% growth in production. At present, Japan is the largest automobile manufacturer in the world, having overtaken the U.S.A. in 1980. However, since 1985, the increasing appreciation of the yen against the U.S. dollar has resulted in diminished profits. This has forced Japanese automobile manufacturers to set up plants in foreign countries, *e.g.*, U.S.A. and Canada. By 1989, over two million Japanese automobiles will be manufactured 'off shore'. Thus, it appears likely that the total production of automotive batteries in Japan will remain unchanged.

Nevertheless, it is equally clear that technological innovation corresponding to savings in size and volume, higher quality, maintenance-free performance, energy conservation, and a wide diversity of customized requirements will be implemented. The recent and remarkable developments in lead/acid technology are aimed at expanding the use of sealed types from the present small units to larger versions suitable for industrial and automotive applications.

References

- 1 Japan Battery and Appliance Industries Association, Statistics.
- 2 Japan Storage Battery Association, Statistics.

- 3 Keiichi Shimizu, Kagaku Kogaku, 49 (1985) 8.
- 4 Kenshou Suematsu, Japan Lead Conference, 1986, Report.
- 5 Japan Storage Battery Association, Standard.
- 6 Hiromichi Ogawa, 4th Advanced Battery Planning Division Meeting, May, 1987.
- 7 Japan Electric Vehicle Association, Technical Document.
- 8 New Energy Development Organization, Technical Document.
- 9 Kansai Electric Power Co., Ltd., Technical Document (GS).